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Distribution and concentration several types of heavy metal correlated with diversity and abundance of microalgae at Tallo Estuary, Makassar, South Sulawesi, Indonesia

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Abstract Tallo estuary is a catchment area river ecosystem is the most affected by aquatic pollution due to a major role of the river for community. A study on water quality, heavy metal concentration and microalgae abundance at selected sites of Tallo River Estuary was carried out. The aim of this research are: 1) Determine distribution and concentration of existing heavy metal at ecosystem of Tallo River Estuary, 2) Identify microalgae dominant from Tallo River Estuary ecosystem where have been polluted by several type of heavy metal.

The results showed that there were three heavy metals at Tallo River Estuary which have a high concentration and above permissible maximum concentration of environment quality standard, such as Lead (Pb), Copper (Cu) and Chromium (Cr). Statistical result showed that there was a significant different in heavy metal concentration between the sampling stations. Concentration of all heavy metals measured was higher at sediment than in the water column.

Skeletonema sp, *Nitzchia sp* and *Synedra sp* were abundance at all sites of the research location. However, there was a strong correlation and significant different between concentration of Chromium in the water and *Skeletonema sp* and *Synedra sp.*
Keywords Diversity and abundance of microalgae; Heavy metal and Tallo River Estuary

Introduction

Estuaries is venerable ecosystem that receive significant anthropogenic inputs from both point and non-point upstream sources and from metropolitan areas, tourism and industries located along the estuarine edges. Estuarine pollution is receiving high attention from the scientific community due to its recognized major source of ecosystem health stress (Kumar and Goyar, 2008) and (Arakel and Tian, 1992). One of main pollutant is entering estuary is heavy metal.

Heavy metal pollution in the estuary has major concern due to they were undegradable element consequently can be either adsorbed onto sediment or accumulated by organisms to toxic level (Begum et al, 2009; Ahmad et al, 2009; Charkhabi et al, 2005). Heavy metals have been introduced into rivers through land surface run off and rainfall precipitation. Other sources such as mine drainage, off shore oil and gas exploitation, industrial (pesticides, paints, leather, textile, fertilizer, pharmaceutical), domestic effluents and acid rain have all contributed to increase metal load to the estuary (Noah and Oomori, 2006) and (Ahmad et al., 2009).

Heavy metals are considered as toxic compounds and their targets are essential metalloenzymes when its present higher than minimum requirement as micronutrient (Erdei, et al., 2005). Accumulating heavy metal in the organism especially plants and microbial can increases in concentration up to 100 to 1000 times those taken up by non- accumulator organisms. Previous researches found that some organisms such as plankton and benthos have a capability to absorb heavy metal in the water and sediment. Those organisms common to be bioindicator and biosorption of heavy metal (Arunakumara and Xuengheng, 2008; Chaala and Zekri, 2005; Wilke et al., 2006; Chojnacka, 2007).

A study was conducted to determine distribution and concentration several types of heavy metal (Lead, Pb; Copper, Cu; Cadmium, Cd; Chromium, Cr and Mercury, Hg) in the Tallo River Estuary which was known to be in the category of polluted water body and to examine whether there is a correlation between the existing type of heavy metal and diversity and abundance of microalgae.

1 Methods

1.1 Study site

The study areas are located at Tallo Estuary on the north coast of Makassar as shown in Figure 1. Tallo Estuary is estuary from Tallo River. Tallo Estuary is the largest estuary in Makassar City and located in South Sulawesi Province. The river originates from northeast of Makassar Bay and its tributaries rise in the forested mountain, which combine of resident, agriculture and industrial activity.

Figure 1 Location of the sampling station on Tallo Estuary in Makassar

Sampling was undertaken along Tallo Estuary, which represented and affected area of industrial, mangrove and domestic activity. A number of 3 sampling stations were identified for heavy metal, microalgae analyses and water quality with triplicate sampling each station.

1.2 Samples Collection and Storage

The water samples were collected from a depth of 1 meter below the surface using Camerer Water Sampler and kept in polyethylene container (500 mL) with the addition of 2 mL concentrated HNO3, in order to preserve the metal. Water sample for microalgae analysis added with 2 mL Lugol's solution as a preservation solution. The sediment samples were collected using Eikman Dredge and kept in the plastic container (1 kg) and put into the cool box. Water quality was measured in situ using Water Quality Checker for dissolved oxygen, pH, conductivity, turbidity, temperature and salinity.

1.3 Heavy Metal and Microalgae Analysis

The heavy metal concentration (Pb, Cu, Cd, Cr and Hg) was analysed using Atomic Absorption Spectrophotometry AAS 1100B model Perkin Elmer.

Microalgae samples were identified and counted using Sedwick Rafter Chamber Method and light microscope with maximum 400 times magnification.

1.4 Statistical Analysis

All sampling were performed in triplicate. Student t-test were carried out to determine significant differences ($p<0.01$) of heavy metal concentration in the sediment and water and also between sampling sites. To examine the correlation between heavy metal concentration and abundance and dominant of microalgae, the data were analyzed using regression analysis in the SPSS v. 15 software program.

2 Results and Discussion

2.1 Water Quality

In general, Tallo River Estuary is characterized by good water quality. Dissolved oxygen concentration in Tallo River Estuary was 5.6 ppm, this concentration is more than minimum requirement for aquatic organism, which is 4 mg/L (Baker, 1980). Tallo River Estuary is the largest estuarine in Makassar. The continuous current created a homogenous condition of DO that was indicated by low standard deviation value. Water clarity of Tallo River Estuary was 0.6 meter, it was considered normal for Tropical estuary. Sampling stations are located within order 5, which is normally affected by human activities and make the waters color to a brownish color. The pH value also classified Tallo River Estuary was a normal pH value for tropical estuary.

Most chemical parameter was detected at low concentration except for phosphate which was found slightly high. The water quality of river depends on catchment and land activities. It has been reported that more than 60% of water quality at aquatic ecosystem is determined by inland activities. Tallo River Estuary

being used by the local community for many purposes such as agriculture, pond, and industrial waste discharge. All activities contributed significantly to increase the phosphate input into the estuary.

2.2 Concentration of heavy metal

Five type of heavy metals that have been analyzed in the water and in the sediment, 3 type of heavy metals, that were Pb, Cd and Cr had high concentration in every research station (Figure 2). Figure 2 shown that concentration all types of heavy metal that have been analyzed was higher in the sediment than in the water column. Statistical analysis indicated that there was a significant difference of concentration 4 types of heavy metals in the water and in the sediment (Pb, Cd, Cu, and Cr), except for Hg there is no significant difference of its concentration between in the water column and in the sediment (Tables 1). Heavy metal concentration in the water and in the sediment varied for every research station. There was three types of heavy metals that had high concentration either in the water or in the sediment at any given research station, such as Lead (Pb), Cuprum (Cu) and Cromium (Cr).

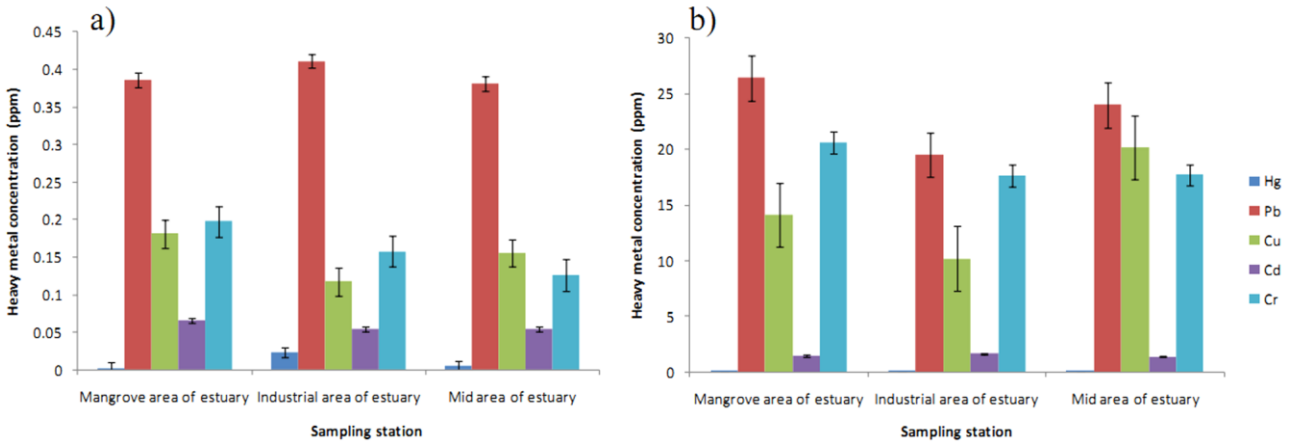

Figure 2 The average of heavy metal concentration (± SE, N=3) in the water and in the sediment from Tallo Estuary. a) The average of heavy metal concentration in the water, b) The average of heavy metal concentration in the sediment

Tables 1 T test result of heavy metal concentration between in the water and in the sediment

Heavy metal	Mean of concentration (ppm)		T test value
	Water	Sediment	
Hg	0.0148	0.0688	0.392ns
Pb	0.3928	23..3084	0.000***
Cu	0.1516	14.8300	0.000***
Cd	0.0586	1.5200	0.000***
Cr	0.1607	18.6942	0.000***

Note: NS is Significant, *** is significant different at $\alpha = 0.05$

Lead (Pb) had the highest concentration at any given research station than others type of heavy metal. Pb concentration was higher in the sediment than in the water column and T test result shown that there was a significant difference of Pb concentration in the water column and in the sediment (Tables 1). High concentration of Pb in the sediment because Pb in the sediment could not be accumulated and degraded, consequently the lead was accumulation at the bottom of the waters, whereas in the water Pb can distribute to respond the action of current (Anggraeni, 2007).

Statistically, there was no significant difference of Pb concentration between research stations either in the water or in the sediment (Tables 1). This result indicated that the distribution of Pb in Tallo Estuary was flattened. This condition could be explained due to strong current at the Tallo Estuary, consequently the pollutant was spreading flattens specially for Pb in all area of the estuary.

Copper (Cu) was the second type of heavy metal that had a high concentration in every research station.

Although there was not significant difference of Cu concentration between in the water and in the sediment (Tables 1), but there was a significant difference of Cu concentration in the sediment among research stations, that was between mangrove area of estuary and mid part of estuary and between industrial area of estuary and mid part of estuary (Tables 2).

Tables 2 Environment quality standard for 5 type of heavy metals

Heavy metal	Maximum conc. of environment quality standard		Reference of EQS
	Conc. in the water (ppm)	Conc. in the sediment (ppm)	
Hg	0.50	0.15	Fabries and Warner (1994)
Pb	0.05	51.0	Fabries and Warner (1994)
Cu	0.03	33.0	Sulawesi Selatan Governer Act No. 14 2003
Cd	0.01	1.00	Sulawesi Selatan Governer Act No. 14 2003
Cr	0.008	10−70	Ministry of Enviroment Act No. 51 2004

Note: EQS : Environment Quality Standard

Third highest heavy metal Concentration from 5 types of heavy metals that were measured was Cromium (Cr). There was a significant difference of Cr concentration between in the water and in the sediment (Tables 1), however T test result showed that there was no significant difference of Cr concentration among research stations either in the water or in the sediment (Tables 2).

Five type of heavy metal were measured from Tallo Estuary, almost all type of heavy metals concentration in the water has been exceeded the maximum permissible concentration of environment quality standard, except for Hg. Those concentration can endanger biota life that existed in the estuary specially microalgae. Whereas concentration of heavy metal in sediment that has exceeded environment quality standard was Cd (Tables 2). Anggraini (2007) found that waters that were influenced by tide the heavy metal concentration in the sediment and in the water will be mobilized.

High concentration of heavy metal concentration Pb, Cu and Cr in Tallo Estuary was caused by some industries that produced waste that contain those types of heavy metal. Shipbuilding Industry (PT. Pelindo) that was in the Tallo Estuary contributed waste that contains the three type of heavy metal. Kumar and Goyal (2008) found that source of heavy metal Pb, Cu, Cr and other heavy metal in territorial water come from mining, industrial area and household waste.

2.3 Abundance and Dominant of Microalgae

Middle side of estuary had the highest microalgae abundance compared to two other research stations (mangrove area and industrial area of estuary) with the average of abundance account for 254 cell/ml, but its station is lowest the number of genera, which was 8 genera/mL (Figure 3). T test result indicated that there is no significant difference of microalgae abundance between stations (Tables 3). However, there is a significant difference of microalgae cell abundance found between industrial area of estuary and mid area of estuary at $P<0.1$.

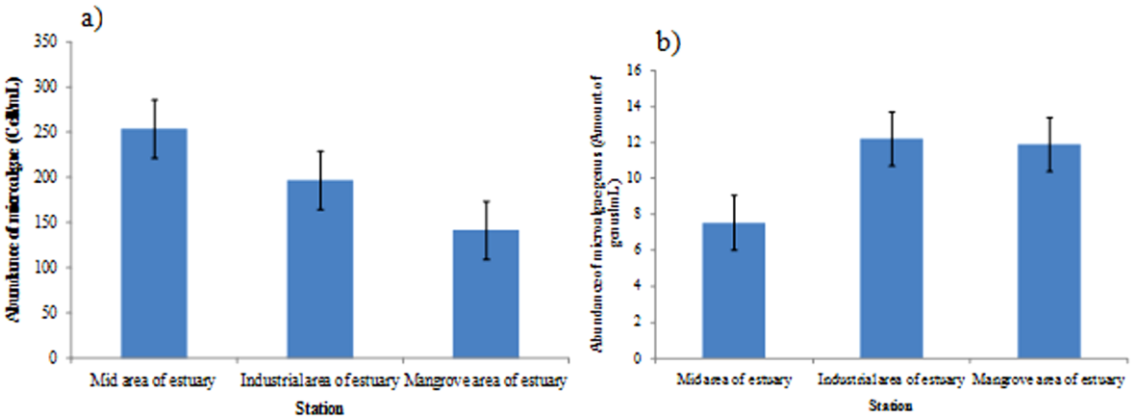

Figure 3 The average of microalgae cell abundance and the number of microalgae species (±SE, N=9) in every research station. a) Microalgae cell abundance in research station, b) The number of microalgae species in research station

Tables 3 T test result of microalgae cell abundance and the number of microalgae species between research station from Tallo Estuary (*: P < 0.1; **: P < 0.05 and ***: P < 0.01; ns : not significant)

Pair Test	Significant Value	
	Abundance of microalgae cell	Richness of microalgae
Mangrove area vs Industrial area	0.592 ns	0.016**
Mangrove area vs Mid area of estuary	0.281 ns	0.03*
Industrial area vs Mid area of estuary	0.55*	0.42 ns

The highest number of genera/species was found in station of industrial area of estuary was 12 genera. Whereas the lowest number of species was found in mid area of estuary. Statistically, there was a significant difference of species number between mangrove area and industrial area of estuary and mangrove area and mid area of estuary. Whereas the number of species between industrial area and mid area of estuary was not differ significantly (Tables 3).

There were three types of microalgae that predominate at three research stations, such as *Skeletonema sp, Nitzchia sp* and *Synedra sp*. Abundance of the three type of microalgae varied in every research station (Figure 4). Skeletonema sp was the most abundance at mid area of estuary with the average of abundance account for 192 cell/ml, whereas for others two species of microalgae the average of abundance was less than 50 cell /ml.

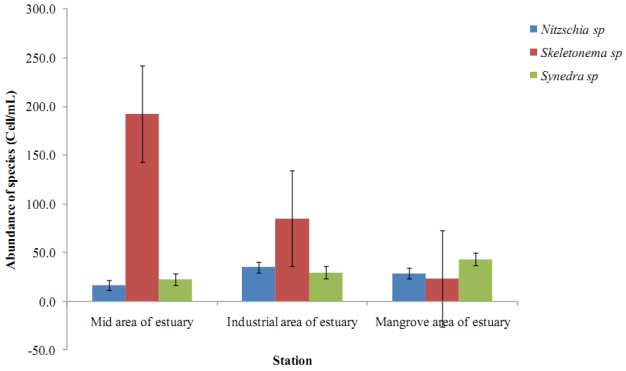

Figure 4 The average of three microalgae dominant (±SE, N= 9) in every research station from Tallo Estuary

2.4 Relationship between heavy metal concentration with abundance and microalgae dominant

Reggression analysis Result between concentration 3 type of heavy metals (Pb, Cu and Cr) in sediment and water column with abundance of three microalgae species dominant (*Nitzchia sp, Skeletonema sp and Synedra sp*) indicated that just a few regression pair that had R^2 value bigger than 0.5 (Tables 4). This condition indicated that microalgae that predominated in Tallo River Estuary had a weak correlatin between concentration of heavy metal that existed in the sediment and in the water. Even though, from this regression result also can be known that there was quite strong regression between heavy metal concentration in the water and particular species, with the R^2 value = 0.915 for regression between Cu and *Nitzchia sp*. Chromium (Cr) had very strong regression and differ significantly with *Skeletonema sp* and *Synedra sp*. This result indicated that some species of microalgae showed a different response to existence of heavy metal in the water column. This result in accordance with research that conducted by Folgar (2008) concentration of heavy metal in the culture media. They also found that species of *Chlorococcum sp* and *Tetraselmis gracilis* grew was pursued by existence of Cd with concentration of 2.5 – 3 mgs/L and 5.0 mgs/L.

Tables 4 Regression analysis result of 3 heavy metals concentration in the sediment and in the water with abundance and microalgae dominant from Tallo River Estuary (* : $R^2 > 0.5$)

Pair Test	Sediment		Water	
	R^2	F-Sig	R^2	F-Sig
Pb vs Richness of microalgae	0.126	0.769	0.997*	0.035
Cu vs Richness of microalgae	0.354	0.595	0.202	0.703
Cr vs Richness of microalgae	0.754*	0.330	0.999*	0.005
Pb vs *Nitzchia sp*	0.886*	0.219	0.421	0.55
Cu vs *Nitzchia sp*	0.050	0.856	0.915*	0.189
Cr vs *Nitzchia sp*	0.772*	0.219	0.484	0.509
Pb vs *Skeletonema sp*	0.237	0.677	0.0001	0.993
Cu vs *Skeletonema sp*	0.222	0.687	0.279	0.646
Cr vs *Skeletonema sp*	0.867*	0.237	0.993*	0.053
Pb vs *Synedra sp*	0.030	0.889	0.114	0.781
Cu vs *Synedra sp*	0.539*	0.475	0.049	0.857
Cr vs *Synedra sp*	0.579*	0.449	0.039*	0.159

3 Conclusions

Tallo River Estuary is characterised by a good water quality except for some physical characteristic that fluctuate as a result of natural annual season changes. However, due to high human activity sarrounding estuary especially industrial activity, Tallo River estuary have been polluted by three main heavy metals, such as Lead, Cuprum and Chromium. Those heavy metal was high at both in the water and sediment. The concentration of heavy metal, especially for Pb, Cu and Cr in the water correlated significantly with abundance of microalgae cell and species. *Skeletonema sp and Synedra sp* have strong correlation with Chromium.

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